Reports

Beryllium-10 Mass Spectrometry with a Cyclotron

Abstract. *The Grenoble cyclotron has been used as a mass spectrometer to measure ratios of beryllium-10 to beryllium-9 of* 10^{-8}, 10^{-9}, *and* 10^{-10} *in standardized beryllium oxide samples. Similar measurements can be used to determine cosmogenic beryllium-10 (half-life,* 1.5×10^{6} *years) profiles in various geophysical reservoirs such as sea sediments and polar ice. This procedure can be used either to date such samples or to give information about geophysical and astrophysical phenomena that have influenced the beryllium-10 production rate in the past.*

There has recently been a great deal of interest in the possibility of using nuclear accelerators as high-sensitivity mass spectrometers. Muller has given a general discussion of the advantages, with particular reference to the Berkeley 88-inch (224-cm) cyclotron (*1*). Using tandem Van de Graaff generators, two groups have demonstrated the feasibility of the method for ^{14}C dating (*2*). A general survey of possible application to trace element analysis, again based on the use of the Berkeley cyclotron, has been described by Stephenson *et al.* (*3*).

The advantage over traditional "counting" methods associated with the use of such a technique for measuring radioactive species increases with the half-life of the nuclide in question. A potentially attractive candidate is therefore the isotope ^{10}Be (half-life, 1.5×10^{6} years) (*4*), which has many astrophysical, geophysical, and cosmochemical applications. In fact, ^{10}Be has been measured by mass spectrometric methods at the Laboratoire René Bernas for a number of years, with a sensitivity comparable to or better than that of counting techniques (*5*). The potential advantages of the accelerator technique as compared to classical mass spectrometry are (i) freedom from interference by species with very similar mass (in this case ^{10}B) by means of absorption or nuclear charge identification and (ii) freedom from interference by "tails" of much more abundant stable isotopes or molecules. We describe here an experiment that we carried out which demonstrates the feasibility of accelerator detection of ^{10}Be with the Grenoble cyclotron.

We made the samples to be analyzed by mixing together aqueous solutions containing a known quantity of ^{10}Be (*6*) and ^{9}Be atoms, such as to give a ^{10}Be/^{9}Be ratio of approximately 10^{-8}, 10^{-9}, or 10^{-10}. The solutions were then reduced in volume by heating, taken to dryness in a quartz crucible, and converted to the oxide with a Bunsen burner. The BeO was crushed to a very fine powder with a mortar, pressed into pellets (5 to 50 mg) with a hydraulic press (8000 kg/cm^{2}), and then sintered by heating under argon to 1800°C. The resulting disks, which were mechanically very solid, were then mounted on a copper plate which was attached so that the BeO was opposite the extraction slit of the ion source of the cyclotron. In this configuration, beryllium ions are sputtered by reflected source gas ions during the out-of-phase portion of the acceleration cycle (*7*).

The ion source was operated with a support gas of neon so that $^{20}\mathrm{Ne}^{4+}$ could be used to simulate $^{10}\mathrm{Be}^{2+}$ in tuning the machine and the beam line. We used an internal beam of ~ 100 nA of $^{9}\mathrm{Be}^{2+}$, although we know from other trials that this current can be increased readily by more than an order of magnitude. The ^{10}Be energy was 30 MeV. Switching between ^{9}Be and ^{10}Be was accomplished by changing the radio frequency of the cyclotron and took less than 5 minutes. The dee voltage was adjusted so as to keep the number of turns of the two isotopes the same. We optimized each beam by making small adjustments in the main field and the trim coils. The ^{10}Be was optimized by means of ^{10}B, which was observed during the experiment in intensities ranging from 10^{4} to 10^{6} particles per second. We made the final ^{10}Be adjustment by varying the main field by an amount corresponding to the known mass difference between ^{10}Be and ^{10}B (6×10^{-5}). The measured resolution of the cyclotron, based on the ^{10}B peak, was 1.1×10^{-4} full width at half maximum. Thus, although ^{10}B and ^{10}Be could not be totally separated this way, there was absolutely no interference from the $^{20}\mathrm{Ne}^{4+}$ (differing in mass by 1.7×10^{-3}), despite its having an abundance $\sim 10^{11}$ larger than ^{10}Be when accelerated.

We detected the ^{10}Be ions by means of a single silicon solid-state detector 50 μm thick and having a surface area of 50 mm^{2}. This detector was mounted on a movable arm inside a reaction chamber, so that it could be remotely positioned at any given angle with repect to the beam. Also mounted in the chamber were foils of aluminum, 6.96 and 13.17 mg/cm^{2}, which could be remotely inserted into the beam. In order to ensure that all the beam would be intercepted by the solid-state detector, a collimator (2 by 4 mm) was placed at the entrance to the reaction chamber. The ^{9}Be intensity was measured both with a Faraday cup positioned behind the reaction chamber and by means of Rutherford scattering off a gold foil which could be inserted into the beam.

In order to separate ^{10}Be from the much larger flux of ^{10}B, we adopted the absorption method outlined by Muller (*1*). Although dE/dx E identification (where dE/dx is the detector that measures the different ionization rates of the different atoms and E is the total energy detector, which follows the dE/dx detector) would also have been possible, we found it was not necessary in the present circumstances. Thus, by inserting the 13.17 mg/cm^{2} aluminum foil in front of the silicon detector, we were able to absorb completely all the ^{10}B while counting all of the ^{10}Be. A more complete description of all the experimental details is given elsewhere (*8*).

The results of our measurements with three different samples are shown in Figs. 1 and 2. We have learned from earlier trials with ^{10,11}B and ^{20,21,22}Ne that the extracted isotope ratio from the cyclotron may differ from the source isotope ratio by as much as a factor of 2. (This may be due to different sputtering, acceleration, or extraction efficiencies.) We therefore prefer to make our measurements relative to a known standard rather than to attempt a determination of the absolute ratio (*9*). Thus, all the results in Fig. 2 have been normalized to the sample having a ^{10}Be/^{9}Be ratio of 9.36×10^{-9}. With such a procedure the two other points differ from the expected values (given by the solid line in Fig. 2) by 30 and 50 percent, respectively.

The two most concentrated ^{10}Be/^{9}Be ratios in Fig. 2 actually represent the average of three and five separate measurements, respectively. In each case, the reproducibility of the measurements (each of which took about 10 minutes for a ^{10}Be

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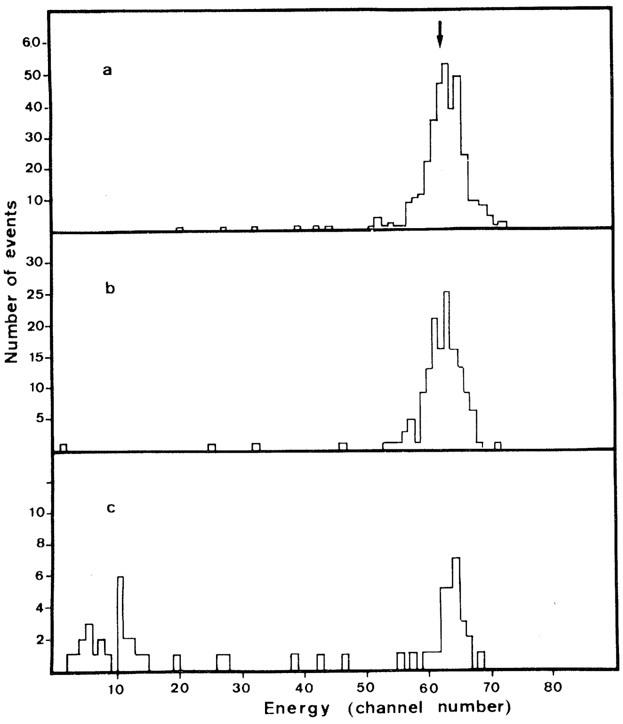

Fig. 1. Examples of energy spectra of detected events for samples having ^{10}Be/^{9}Be ratios of (a) 9.36 × 10^{-9}, (b) 7.86 × 10^{-10}, and (c) 8.46 × 10^{-11}. The arrow indicates the calculated energy for ^{10}Be nuclei after traversing the aluminum absorber. The recording times were 5 minutes for (a) and (b) and 10 minutes for (c).

and ^{9}Be determination) was within the statistical accuracy (5 to 10 percent) of the number of ^{10}Be atoms counted.

The time necessary to change samples in the ion source was about 3/4 hour and of course necessitated displacing the ion source. It is probably the difficulty in repositioning the ion source in exactly the same geometry that accounts for a larger deviation between samples than for replicate measurements with the same sample. The lowest concentration point in Fig. 2 was based on a total of only 27 ^{10}Be events and thus has a large statistical error.

Unfortunately, a problem with the ion source forced us to terminate the experiment before we had a chance to measure our "blank" (^{10}Be/^{9}Be = 0) sample. We are thus unable to give any precise value for the ^{10}Be detection limit under the above conditions. However, using our minimum measured ratio (^{10}Be/^{9}Be = 8 × 10^{-11}) and a very conservative upper limit for the amount of sample actually consumed during the measurement (1 mg of BeO), we obtain a detection limit of ~2 × 10^{9} atoms of ^{10}Be. An examination of the background counts on either side of the ^{10}Be peak in Fig. 1c suggests that the actual limit is one to two orders of magnitude lower than this. Identification by a *dE*/*dx E* telescope would undoubtedly improve this value still more. Thus we believe that the eventual analysis of samples containing 10^{7} atoms of ^{10}Be is a completely realistic objective. This limit is about three orders of magnitude lower than could ever be achieved by counting techniques (*10*). However, even at the demonstrated level of 10^{9} atoms, very exciting new investigations are possible, as discussed briefly below.

The cosmogenic production rate of ^{10}Be in the atmosphere is ~1.5 × 10^{-2} atom cm^{-2} sec^{-1} (*11*). This ^{10}Be accumulates in geophysical reservoirs, such as ocean sediments or polar ice, where it can thus preserve a record of these cosmic-ray interactions over the past 2 × 10^{7} years (*12*). The most obvious advantage of a more sensitive ^{10}Be detection technique is the capability of dating older or smaller samples, or both, from such reservoirs. This subject has been discussed by Muller (*1*). He has emphasized that, for samples several half-lives old, even the rather modest accuracy achieved in the present work can give quite accurate results. For example, a typical ^{10}Be/^{9}Be ratio in a "fresh" ocean sediment is 1 × 10^{-8}. Our measured ratio of 8 × 10^{-11} would thus correspond to such a sample after 10^{7} years, and our 50 percent error in the measured ratio would translate into an error of less than 10 percent in this deduced age.

Use of ^{10}Be in the above manner implies a knowledge of the initial ^{10}Be abundance (or ^{10}Be/^{9}Be ratio) in the sample. The assumption most commonly made is that this initial abundance is the same as that found in contemporary samples from similar reservoirs. In other words, one assumes a constant ^{10}Be production rate. An alternative, and to our minds even more interesting application of the ^{10}Be method, is to investigate variations in this production rate. Such variations can be produced by changes in solar activity or in the geomagnetic field (both of which modulate the galactic cosmic rays) or by variations in the galactic cosmic-ray intensity itself [for example, possible enhancements due to "local" supernova (*13*)]. It has also been suggested that, even with a constant production rate, climatic conditions might vary the ^{10}Be deposition rate by depositing into the oceans large quantities of ^{10}Be previously stored in ice flows (*11*).

An ocean sediment core having a diameter of 10 cm will contain about 5 × 10^{10} atoms of ^{10}Be for each 10^{3} years of accumulation [finer time resolution in such sediments is difficult to achieve because of bioturbation or ocean mixing times (*14*)]. Assuming for the moment a concentration of 10^{9} atoms of ^{10}Be for analysis, profile measurements with this 10^{3}-year resolution are thus possible back to about 8 × 10^{6} years. Such measurements might, for example, permit one to see variations in cosmic-ray intensities during geomagnetic reversals, which are believed to take place on a time scale of less than 10^{3} years (*11*).

The deepest available polar ice cores offer a continuous record back to about 10^{5} years (*15*). It should be possible to exploit a much finer time scale in these cores than in sediments. Here again, with a core 10 cm in diameter and 10^{9} atoms of ^{10}Be as a basis, a time resolution of ~20 years is possible. Thus, some of the shorter-term variations in solar activity that have recently been suggested (*16*) can be investigated. In this regard, ^{10}Be has significant advantages over ^{14}C. Not only has it a much longer half-life (thus permitting one to study such variations much farther into the past), but, unlike the case of carbon,

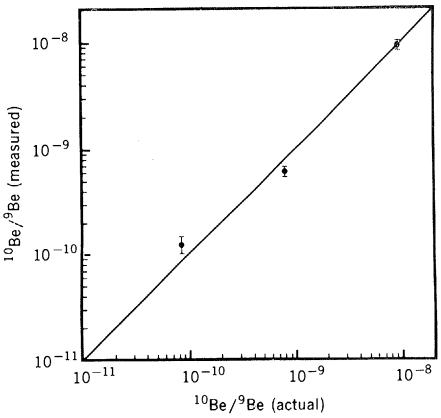

Fig. 2. Measured versus actual ^{10}Be/^{9}Be ratios for the three samples tested. The absolute value of the measured ratios have been normalized to the point in the upper right-hand corner, as indicated in text. Errors indicated are statistical (1 standard deviation) only.

there are no large equilibrium reservoirs of beryllium to "dampen" out effects due to rapid fluctuations in the production rate.

As has been emphasized by Somayajulu (*11*), the search for effects of the type described above necessitates an independent method of determining the accumulation rates for the reservoirs in which the ^{10}Be is measured. It also requires the analysis of a fairly large number of samples and, depending on the magnitude of the variations being sought, probably requires an accuracy of the order of 20 percent. This requirement suggests the desirability of certain modifications in our technique. Probably the most important of these would be some method of rapidly changing samples, without changing any parameters of the accelerator. Not only would such a modification permit a much shorter measurement time per sample, but it also might permit one to bypass the acceleration of the ^{9}Be completely and simply compare ^{10}Be intensities between the sample and a known standard. On the basis of our replicate determinations of the same sample, we expect that such a procedure would improve the accuracy of the measurements considerably. Fortunately, the Grenoble cyclotron is equipped with an external ion source, and it may be possible to use this ion source to solve this problem.

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References and Notes

1. R. A. Muller, *Science* **196**, 489 (1977).
→ D. E. Nelson, R. G. Korteling, W. R. Stott, *ibid.* **198**, 507 (19 → C. L. Bennett, R. P. Beukens, M. R. Clover, H. E. Gove, R. B. Liebert, A. E. Litherland, K. H. Purser, W. E. Sondheim, *ibid.*, p. 508.
3. E. J. Stephenson, D. J. Clark, R. A. Gough, W. R. Holley, A. Jain, *Nucl. Instrum. Methods* **152**, 477 (1978).
4. F. Yiou and G. M. Raisbeck, *Phys. Rev. Lett.* **29**, 372 (1972).
5. F. Yiou, M. Baril, J. Dufaure de Citres, P. Fontes, E. Gradsztajn, R. Bernas, *Phys. Rev.* **166**, 968 (1968); P. Fontes, C. Perron, J. Lestringuez, F. Yiou, R. Bernas, *Nucl. Phys. A* **165**, 405 (1971).
6. The ^{10}Be was made by the ^{13}C(n,α)^{10}Be reaction [D. R. Goosman, *Nucl. Instrum. Methods* **116**, 445 (1974)] and was provided to G.M.R. and F.Y. by D. Goosman several years ago for an analysis of the ^{10}Be/^{9}Be ratio. We determined the absolute ^{10}Be concentration by isotope dilution, using a mass spectrometer (G. M. Raisbeck, J. Lestringuez, F. Yiou, unpublished results).
7. E. D. Hudson, M. L. Mallory, R. S. Lord, *IEEE Trans. Nucl. Sci.* **NS-23**, 1065 (1976).
8. G. M. Raisbeck, F. Yiou, M. Fruneau, J. M. Loiseaux, in preparation.
9. In the present experiment there was, in fact, some ambiguity in the absolute ^{10}Be/^{9}Be values. The results derived based on the use of the ^{9}Be current obtained by Rutherford scattering were within 15 percent of the normalized values given in Fig. 2, whereas those obtained based on the use of the ^{9}Be from Faraday cup measurements were lower by almost a factor of 5. Although we originally attributed this difference to an incorrectly calibrated Faraday cup, more recent experiments suggest that the low ratio may result from our procedure of using ^{20}Ne^{4+} to tune the beam line. Apparently even the small ($\sim 10^{-3}$) mass difference between ^{20}Ne^{4+} and ^{10}Be^{2+} is sufficient to affect the beam line transmission. This difficulty could be avoided if ^{10}B^{2+} instead of ^{20}Ne^{4+} were used to tune the beam line. The discrepancy between the ^{9}Be from the Rutherford scattering and from the Faraday cup would, of course, still remain unexplained. What is important to us is that the ratio of these two measurements remained constant throughout the experiment, thus giving us confidence that our relative isotope ratios are reliable.
10. S. Tanaka, T. Inoue, and M. Imamura [*Earth Planet. Sci. Lett.* **37**, 55 (1977)] have recently extended the ^{10}Be counting technique to essentially its natural limit. These workers have been able to construct a beta counter having a background of eight counts per day. Taking typical values for chemical yield (50 percent) and counter efficiency (40 percent), this corresponds to the count rate of a sample containing $\sim 3 \times 10^{10}$ atoms of ^{10}Be. For an activity equal to this background, it is necessary to count for 1 week in order to have 1-standard-deviation statistics of 20 percent. Even if the background could be eliminated completely, this limit would not change appreciably.
11. B. L. K. Somayajulu, *Geochim. Cosmochim. Acta* **41**, 909 (1977).
12. D. Lal and B. Peters, in *Handbuch der Physik*, K. Sitte, Ed. (Springer, Berlin, 1967), vol. 46/2, p. 551.
13. J. C. Higdon and R. E. Lingenfelter, *Nature (London)* **246**, 403 (1973).
→ N. J. Shackleton, *Philos. Trans. R. Soc. London Ser. B* **280**, 169 (1977).
15. S. G. Johnsen, W. Dansgaard, H. B. Clausen, C. C. Langway, Jr., *Nature (London)* **235**, 429 (1972).
16. J. A. Eddy, *Science* **192**, 1189 (1976).

29 March 1978; revised 14 June 1978

Apparent Saturation of Blue-Sensitive Cones Occurs at a Color-Opponent Stage

Abstract. *Response saturation of blue-sensitive cone pathways was studied by measuring increment thresholds for violet test flashes on flashed violet fields in the presence of a steady yellow "auxiliary" field of constant radiance. Adding intense yellow field flashes to the violet field flash could eliminate or reduce response saturation (greatly reduce threshold), whereas "negative" yellow field flashes drove the mechanism to further saturation. The response saturation is thus not, in general, controlled exclusively by independent blue-sensitive cones but by spectrally opponent mechanisms that receive opposite-signed signals from blue-sensitive cones and from green- or red-sensitive cones. These results add to a growing number of studies that demonstrate that detection of signals from blue-sensitive cones is largely through a color-opponent pathway.*

The human visual system has limited dynamic response and will saturate when sufficiently stimulated. The rod monochromat who possesses only rod photoreceptors, for example, cannot see patterns on a field more intense than about 1000 scotopic trolands (*1*) because the rod pathways saturate and therefore cannot signal intensity variations. Aguilar and Stiles (*2*) demonstrated saturation of the "rod mechanism" in normal observers with a steady red adapting field and green test flashes presented on the peripheral retina. The intensity of the test flash was measured as a function of field intensity. The resultant increment threshold curve became very steep at field intensities of ~2000 to 5000 scotopic trolands, demonstrating saturation. Electrophysiological studies on rat (*3*) and *Necturus* (*4*) show saturation of the photocurrent of rod receptors. It is thus plausible that saturation of human rod pathways occurs at a very early stage of the visual system—in the rods themselves.

Saturation of human cone pathways has also been shown by increment threshold curves obtained with a flashed test spot on a flashed field (*5*). At sufficient intensity of the flashed field, the test flash becomes invisible even when much more intense than the field. This saturation is typically not observed when the field is presented continuously; the threshold simply rises to a high level in proportion to the adapting field intensity (*6*). Mollon and Polden (*7*), however, have shown that the blue-sensitive cone pathways do saturate with steady violet adapting fields.

Our results show that the saturation of the blue-sensitive cone pathways does not, in general, occur within independently acting blue-sensitive cones. Response saturation is studied with flashed fields. According to the principle of univariance (*8*), the response of independent photoreceptors would be controlled by the rate of quantum absorption and not by the wavelength of light. Thus if the response saturation were to occur directly in such independent photoreceptors, flashes of any color would simply drive the mechanisms into further saturation. Our results are in the opposite direction: positive yellow field flashes may undo the saturation produced with violet field flashes, and negative yellow flashes may promote this saturation. This re-

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